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Photo-crosslinking Permanent Optical Storage Devices using Biocompatible Kojic Acids

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Abstract—Biocompatible kojic acids incorporated in azodye molecules were studied with the illumination of UV light. Study revealed the novel photo crosslinking effect where kojic acid-azodye molecules crosslink themselves with the light which allow molecules to create permanent optical storage devices. Obtained results are very useful for the electronic industry because of cost effective approach and easy to crosslink nature.

Keywords—*photocrosslink; azodyes; crosslink; photoisomerization; optical storage device*

I. INTRODUCTION

Kojic acids are organic acid and by-product of fungi during aerobic fermentation process. The name of kojic acid was derived from ‘koji’, the common name of fungus *Aspergillus oryzae* which is the starter culture or inoculum used to obtain kojic acid from food fermentation. Crystalline kojic acid was firstly isolated by Saito, Japan, in the year 1907, from fermentation on steamed rice [1]. Kojic acid crystalizes in form of colorless. The natural origin of kojic acid ensures it to be a non-hazardous biological derivative and biodegradable compound.

The utilization of kojic acid from the fungi fermentation has been highly recommended to make it into useful applications. Since 1995 when Charles Pfizer and company, USA, attempted to manufacture kojic acid [2], the demand of kojic acid has been growing rapidly. It is widely applied in food industry as well as in cosmetic industry. In chemical industry, it is used in preparation of ethers, esters, azodyes and other important compounds. Also, kojic acid possesses its antibiotic properties against Gram-negative and Gram-positive bacteria for medical usage.

On the other hand, azodye has been a hot topic of research due to their photoisomerization and photochromic properties [3]. Upon UV irradiation (around 365 nm, corresponding to the π - π^* excitation of the azo group), the energetically more stable *E* or *trans* configuration, with elongated rod-like molecular form, changes into a bent *Z* or *cis* configuration. The reverse transformation occurs with visible irradiation (in the range of 400 nm – 500 nm, equivalent to that of n - π^* transition). The

later change can also occur in the dark by a process called ‘thermal back relaxation’.

Photoinduced phenomenon in which incident light brings about molecular ordering/disordering of liquid crystalline system is being proposed as future technology for optical storage device [4]. The heart of the phenomenon in such system is nothing but the reversible photoisomerization of the molecule containing photochromic azodyes [5]. Many azodyes have been reported that they took from few hours to few days for return back to their original *trans* configuration [6]. However, the long thermal back relaxation is required for making a permanent optical storage device such that the compound stay in *cis* configuration for long time. Here, we attempt to make a permanent optical storage device using biocompatible kojic acids incorporated in azodye molecules. The compound is expected to remain in *cis* configuration so that pattern generated on the device can be store permanently.

In this work, photoisomerization behavior of kojic acid-azodyes with the effect of photopolymerization of monomer and photo-crosslinking of polymer were studied. Results showed that molecule never relax back to its original state when left in the dark for more than 100 minutes. This result is useful for creating permanent optical storage device.

II. EXPERIMENTAL DETAILS

A. Structure

The chemical structure of the kojic acid incorporated in azodyes molecule named as CZ2 is shown in Fig. 1.

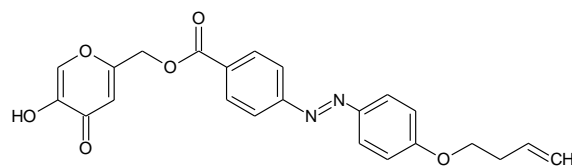


Fig. 1. Chemical structure of *trans* kojic acid-azodyes (CZ 2)

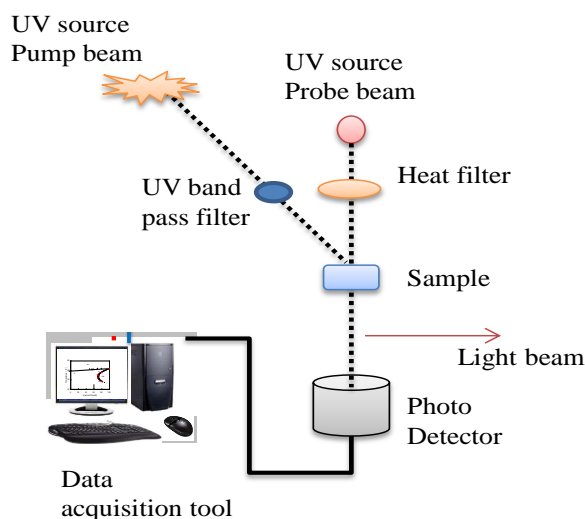


Fig. 2. Experimental set up for photoisomerization study in dark condition

B. Sample Preparation

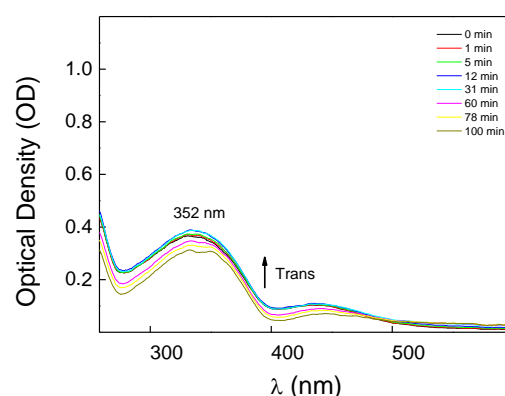
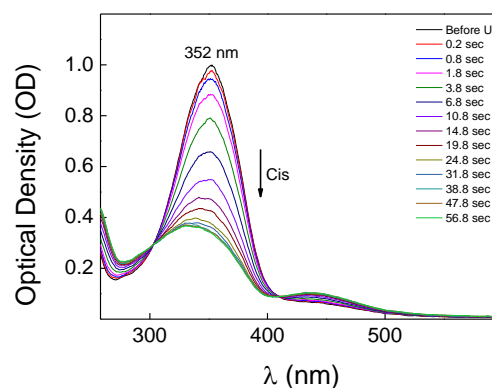
Photoisomerization study was performed using an Ocean Optics HR-2000+ UV-Vis spectrophotometer. Detail experimental set up used for this study is shown in Fig.2. The compound CZ2 were dissolved in methanol at concentration, $C = 1.2 \times 10^{-5} \text{ mol L}^{-1}$ and measured under air in the dark room with room temperature ($27 \pm 1^\circ\text{C}$) using 1 cm quartz cuvettes. The cuvettes were closed to avoid the evaporation of the solvent and the solutions were not disturbed during the irradiation with Hamamatsu light ($\lambda = 365 \text{ nm}$) using suitable filter UG11. Heat filter was inserted to avoid any heating effects. Intensity passed through the filter was measured to be 5 mW/cm^2 .

III. RESULTS AND DISCUSSION

The compound CZ2 contains a photosensitive group and a polymerizable group. The $-\text{N}=\text{N}-$ double bond belongs to azobenzene which responsible for *E/Z* isomerization when light is shined. One terminal end of the molecule is attached with kojic acid while another end attached to ethene. This compound can be dissolved in polar solvent such as ether, ethanol and methanol. It is less soluble in chloroform. The compound shows strong adsorption at 352 nm.

Photoisomerization studies were performed on solutions and also on solids give an idea of the materials behavior with respect to UV light and also these results are indispensable for creating optical storage devices. Upon UV illumination, the peak absorption at 352 nm decreased due to $\pi-\pi^*$ electron transition of azo group, followed by slight increase in the peak around 450 nm as a result of $n-\pi^*$ electron transition. The *trans* isomers took about 56 seconds to convert to *cis* isomers completely (See Fig.3, top). After 56 seconds, there was no changes in the absorption spectra confirm saturation of the *E/Z* isomerization process. The conversion efficiency (*CE*) of the *E-Z* photoisomerization is estimated from eq. 1.[7]

$$CE = \frac{A(t_0) - A(t_\infty)}{A(t_0)} \times 100\% \quad (1)$$



Where $A(t_0)$ is absorbance before UV and $A(t_\infty)$ is absorbance after UV. CZ2 studied in solution give 66.25% in conversion efficiency.

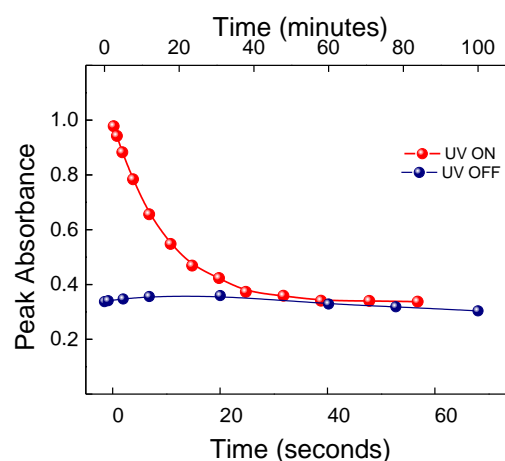


Fig. 4. Absorption spectra when UV on (top) and UV Off (bottom) takes place as a function of exposure and recovery time. Data extracted from Fig.3.

Just after photo saturation, the solution was left in the dark to allow thermal back relaxation to occur, which leads to *cis* isomer transform to *trans* isomers as shown in Fig.3 (bottom).

But surprisingly in this case, system never returns back to the original configuration. Reason for the surprising behavior is discussed in detail in later sections. Here spectral data were recorded at subsequent time intervals. Fig. 4, which is extracted from fig.3 shows the *E/Z* and *Z/E* transformation as a function of exposure/recovery time. Data suggests that system needs 56 seconds to change from *trans* to *cis* whereas *cis-trans* never take place emphasizing the light effect on photosaturated compounds.

In order to fabricate a device, solid study is necessary to confirm the compound stability in photoisomerization behavior within a solid cell. The solid cell was prepared by adding 5 wt% of CZ2 into 95 wt % of liquid crystal. The mixture was filled into sandwiched ITO coated glass plates with previously rubbed substrates. Photoisomerization behavior was observed

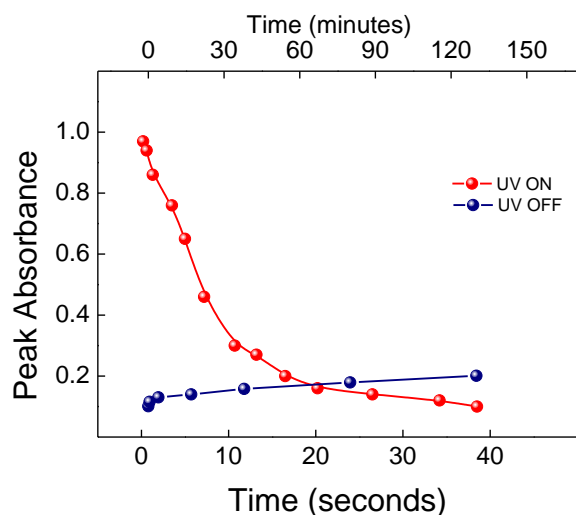


Fig. 5. Spectral measurement result of 5% wt. CZ2 in solid cell study before and after UV illumination

when UV light at wavelength 365 nm was illuminated at the solid cell. The result shows that photosaturation occurs around 40 seconds whereas as even after 2 hours also system never recovers to original *trans* state. That means somehow system becomes locked after photosaturation is achieved.

Although there is not clear evidence for this unusual and surprising behavior but we are trying to elucidate the possible reason. The possible reason for observing this situation is because polymerization of ethene group in CZ2, followed by photo-crosslinking effect. Exposing the material to light, initiate photopolymerization reaction, thousands of structural unit join together become photopolymer of kojic acid-azodyes. Then, each photopolymer chain are capable to link together by formation of interchain bonds under the influence of light along with neighboring liquid crystal molecules which prevents the host liquid crystal molecules to go back to the original *trans* configuration. Entire system is photocrosslinked and as a result the *cis* configuration could never relax to the original *trans* configuration.

Cartoon diagram showing the above mentioned reason is given in Fig.6. Where host liquid crystal molecules were mixed with guest kojic acid based azobenzene molecules and then light of suitable wavelength is shined on them. System transfers from energetically more stable *trans* configuration to unstable *cis* configuration. As a result of which reverse transformation should take place but here in this case due to photocrosslinking effect system never relax back to original *trans* configuration.

storage device was constructed based on the principle described in this article and observed under the crossed polarizers. Initially the compound CZ2 was added to liquid crystals (like a guest-host effect) inside the device and then 'advance' mask was placed on the top. When light of wavelength 365 nm was shined through mask, the 'advance' pattern was generated. A dark region is due to the liquid crystal transition from order to disorder (illuminated region) and a bright birefringence region is the masked region which are

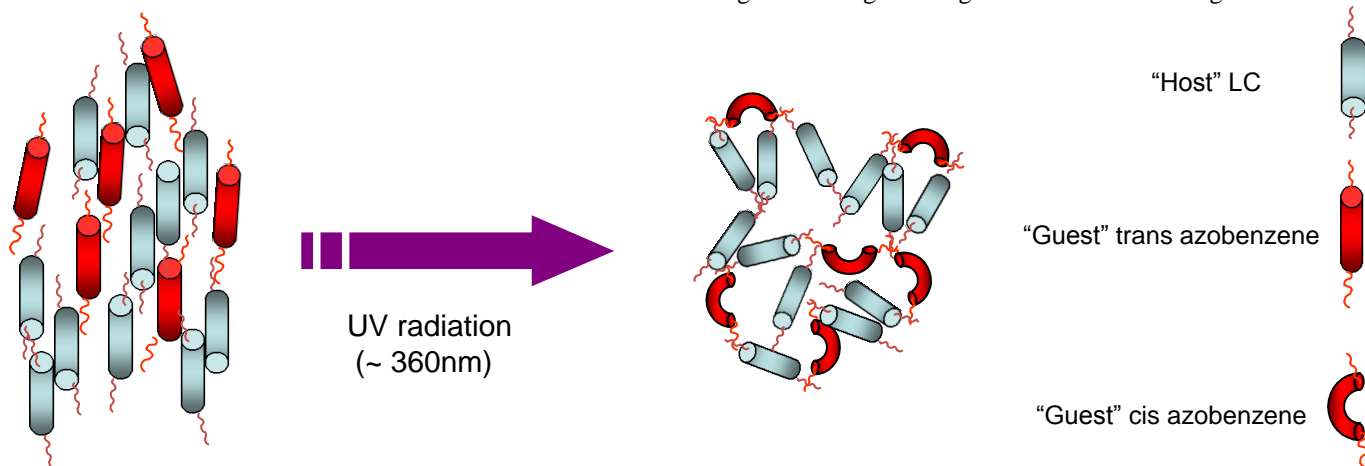


Fig.6. Cartoon diagram model showing the photocrosslinking effect observed in the presented molecules. System never goes back to the original configuration due to strong cross linking effect.

shown in Fig. 7. The device can function for a long term due to photo-crosslinking effect.



Fig.7: Demonstration of the permanent optical storage device made up of kojic acid based azobenzene moiety exhibiting photocrosslinking effect. Bright regions were masked and dark regions were illuminated. System changes from order to disorder transition.

IV. CONCLUSION

Photoisomerization study of kojic acid incorporated into azodye molecules is presented. This result showed novel method of creating permanent optical storage device achieved by using kojic acid-azodyes when photopolymerizable ethene group at the terminal end expose to light. The effect of photopolymerization and photo-crosslinking play a crucial role to maintain molecule in *cis* configuration for long time resulting in permanent optical storage device.

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